

# PATENT SPECIFICATION

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The inventor of this invention in the sense of being the actual deviser thereof within the meaning of Section 16 of the Patents Act, 1949, is FRANCOIS ESCHARD, a French citizen, of 86 bis Boulevard Latour-Maubourg, Paris, France.

## COMPLETE SPECIFICATION

### Improvements in or relating to the Production of Olefinic Compounds by the Continuous Catalytic Dehydration of Alcohols in the Liquid Phase

We, INSTITUT FRANCAIS DU PETROLE, DES CARBURANTS ET LUBRIFIANTS, a French Body Corporate, of 2 rue de Lubecq, Paris, XVI, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with improvements in or relating to the production of olefinic compounds by the continuous acid catalysed dehydration of alcohols in the liquid phase. The expression "olefinic compounds" is used in the present specification to refer to compounds containing an olefinic double bond; it includes, therefore, olefines themselves, that is compounds of the general formula  $C_nH_{2n}$ , cycloalkenes and aromatic compounds containing an olefinic double bond in a side-chain, such as styrene.

We have found that if this process is carried out in the presence of a polar solvent in which the alcohol is soluble and which has a higher boiling point than the products of the reaction, namely the olefinic compound produced and water, the activity of the catalyst is increased and accordingly the amount of catalyst employed may be considerably reduced or catalysts of weak activity, such as phosphoric acid, may be employed. The advantage of such catalysts of weak activity, for example, phosphoric acid, is that they do not decompose under the reaction conditions and do not promote side reactions such as polymerisation and isomerisation.

According to the present invention, therefore, there is provided a method for the continuous production of olefinic compounds by the acid catalysed dehydration of alcohols in the liquid phase, wherein the dehydration is

carried out in the presence of a polar solvent in which the alcohol to be dehydrated is soluble and which has a higher boiling point than that of water and of the olefinic compound produced.

The catalytic dehydration is preferably carried out by heating a mixture of an acid dehydrating catalyst, the polar solvent and an alcohol to boiling point, removing the reaction products (olefinic compounds and water) by distillation and continuously adding additional alcohol to the reaction mixture to maintain the reaction volume substantially constant.

In order to minimise reaction between the catalysts and the olefinic compounds produced, which leads to the production of high molecular weight by-products, the concentration of olefinic compound in the reaction mixture should be maintained as low as possible.

Suitable polar solvents for use in the method according to the invention include phenols (for example phenol, cresol and xylenol), phenol derivatives, nitro-aromatic derivatives (for example nitrobenzene and nitrotoluene) and acetic acid and its derivatives, particularly the halogenated derivatives thereof such as mono- and di-chloroacetic acids and the corresponding fluoroacetic acids.

The use of polar solvents in accordance with the present invention results in high yields of olefinic compounds being obtained from the alcohols employed with a low concentration of catalyst, and in particular in a considerable increase in the rate of reaction.

As will be seen from the following table a higher yield of olefinic compound is obtained from any given alcohol with a lower concentration of catalyst when the dehydration is carried out in the presence of a polar solvent:

## CONTINUOUS DEHYDRATION OF CYCLOHEXANOL

Temp. in degrees C.	Catalyst	Concentration of catalyst (gms./litre)	Solvent	% Solvent by vol.	Total vol.: (cc)	Yield of olefinic compd. (cc/minute)
169	H <sub>3</sub> PO <sub>4</sub>	160	None		250	0.33
168	H <sub>3</sub> PO <sub>4</sub>	200	None		200	0.4
165	H <sub>3</sub> PO <sub>4</sub>	62.5	Phenol	75	400	6
165	H <sub>3</sub> PO <sub>4</sub>	55.5	Phenol	55.5	450	5
160	<i>p</i> -CH <sub>3</sub> .C <sub>6</sub> H <sub>4</sub> .SO <sub>3</sub> H	17.5	None		250	0.44
158	<i>p</i> -CH <sub>3</sub> .C <sub>6</sub> H <sub>4</sub> .SO <sub>3</sub> H	1.75	Phenol	85	250	1.6
158	<i>p</i> CH <sub>3</sub> .C <sub>6</sub> H <sub>4</sub> .SO <sub>3</sub> H	1.75	Phenol	50	250	0.72
160	H <sub>2</sub> SO <sub>4</sub>	5	None		300	0.5
163	H <sub>2</sub> SO <sub>4</sub>	5	Phenol	14.3	300	2
140	H <sub>3</sub> PO <sub>4</sub>	62.5	Nitrobenzene	75	400	8
164	<i>p</i> -CH <sub>3</sub> .C <sub>6</sub> H <sub>4</sub> .SO <sub>3</sub> H	9	Nitrobenzene	25	250	0.29
145	H <sub>3</sub> PO <sub>4</sub>	240	Acetic acid	50	250	2.92
145	H <sub>3</sub> PO <sub>4</sub>	240	Acetic acid	85	250	3.79
165	H <sub>3</sub> PO <sub>4</sub>	80	Monochloro- acetic acid	50	250	4.25
DEHYDRATION OF SECONDARY OCTYL ALCOHOL						
174	H <sub>3</sub> PO <sub>4</sub>	55.5	Phenol	55.5	450	7
175	H <sub>3</sub> PO <sub>4</sub>	55.5	Phenol	44.5	450	3.5
DEHYDRATION OF PRIMARY OCTYL ALCOHOL						
210	H <sub>3</sub> PO <sub>4</sub>	111	Phenol	55.5	450	1

The rate of reaction, and in consequence the yield of olefinic compound obtained, depends, for a given concentration of catalyst, on the percentage of solvent employed.

In order that the invention may be more clearly understood the following Examples are given by way of illustration only.

## EXAMPLE 1:

- 10 Dehydration of cyclohexanol by phosphoric acid in the presence of phenol.

15 A mixture of H<sub>3</sub>PO<sub>4</sub> (28.5 gms.; 0.291 mol.), phenol (235 gms.; 2.5 mols.) and cyclohexanol (100 gms.; 1 mol.) was heated to boiling point (165° C.) at atmospheric pressure and the reaction products removed by distillation. Cyclohexanol (315 gms.; 3.15

mols.) was continuously added to the reaction mixture during distillation to maintain the reaction volume constant. 255 gms. (3.10 mols.) of cyclohexene were produced per hour, representing a yield of 98.5% of the theoretical yield.

## EXAMPLE 2:

Dehydration of cyclohexanol by phosphoric acid in the presence of phenol.

A mixture of H<sub>3</sub>PO<sub>4</sub> (7 gms.; 0.0715 mol.), phenol (255 cc.; 2.9 mol.) and cyclohexanol (45 cc.) was heated to boiling point (176° C.). The proportion by volume of phenol in the mixture (85% by volume of phenol) was that which gives rise to the maximum rate of reaction with respect to the weight of catalyst

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employed. In order to maintain the reaction volume constant, cyclohexanol at a temperature of 176° C. was continuously introduced into the reaction mixture at the rate of 97

5 gms. (0.97 mol.) per hour. 76.5 gms. (0.93 mol.) of cyclohexene were obtained per hour, representing a yield of 96% of the theoretical yield.

#### EXAMPLE 3:

10 Dehydration of cyclohexanol by sulphuric acid in the presence of phenol.

A mixture of  $H_2SO_4$  (1.5 gms.), phenol (43 cc.; 0.45 mol.) and cyclohexanol (250 cc.) was heated to boiling point (163° C.) at atmospheric pressure. Cyclohexanol was continuously introduced into the reaction mixture in order to maintain the reaction volume constant at a rate of 125 gms. (1.25 mol.) per hour. 130 gms. (1.18 mol.) of cyclohexene were obtained per hour, representing a yield of 95% of the theoretical yield.

#### EXAMPLE 4:

Dehydration of cyclohexanol by phosphoric acid in the presence of nitrobenzene.

25 A mixture of phosphoric acid (25 gms.), nitrobenzene (308 gms.) and cyclohexanol (100 gms.) was heated to boiling point (140° C.) at atmospheric pressure. In order to maintain the reaction volume constant, cyclohexanol was continuously introduced into the reaction mixture at a rate of 500 gms. (5 mol.) per hour. Cyclohexene and water were eliminated by distillation as they were formed. 402 gms. (4.9 mol.) of cyclohexene were thus obtained per hour, representing a yield of 98% of the theoretical yield.

#### EXAMPLE 5:

Dehydration of secondary octyl alcohol by phosphoric acid in the presence of phenol.

40 A mixture of phosphoric acid (25 gms.; 0.255 mol.), phenol (141 gms.; 1.5 mol.) and secondary octyl alcohol (250 cc.; 1.6 mol.) was heated to boiling point (175° C.) at atmospheric pressure. In order to maintain the reaction volume constant, secondary octyl alcohol was continuously introduced into the reaction mixture at a rate of 340 gms. (2.6 mol.) per hour. 281 gms. (2.51 mol.) of octene were thus obtained per hour, representing a yield of 96.2% of the theoretical yield.

#### EXAMPLE 6:

Dehydration of primary octyl alcohol by phosphoric acid in the presence of phenol.

55 A mixture of phosphoric acid (25 gms.; 0.255 mol.), phenol (235 gms.; 2.5 mol.) and octyl alcohol (200 cc.; 1.27 mol.) was heated to boiling point (210° C.) at atmospheric pressure. Octyl alcohol was continuously introduced into the reaction mixture at a rate of 34 gms. (0.262 mol.) per hour in order to maintain the reaction volume constant. 28.8 gms. (0.258 mol.) of octene were thus obtained

per hour, representing a yield of more than 98% of the theoretical yield.

#### EXAMPLE 7:

Dehydration of cyclohexanol by *p*-toluene-sulphonic acid in the presence of phenol.

A mixture of *p*-toluene-sulphonic acid (0.44 gms;  $0.231 \times 10^{-2}$  mol.), phenol (212 cc.) and cyclohexanol (38 cc.) was heated to boiling point (158° C.) at atmospheric pressure. The proportion by volume of phenol in the mixture (85% by volume of phenol) was that which gives rise to the maximum rate of reaction with respect to the quantity of catalyst employed. Cyclohexanol at a temperature of 158° C. was continually introduced into the reaction mixture at a rate of 96.5 gms. (0.965 mol.) per hour in order to maintain the reaction volume constant. 78 gms. (0.95 mol.) of cyclohexene were thus obtained per hour, corresponding to a yield of 98.5% of the theoretical yield.

#### EXAMPLE 8:

Dehydration of cyclohexanol by *p*-toluene-sulphonic acid in the presence of nitrobenzene.

A mixture of *p*-toluene-sulphonic acid (2.25 gms.;  $1.18 \times 10^{-2}$  mol.), nitrobenzene (125 cc.) and cyclohexanol (125 cc.) was heated to boiling point (164° C.) at atmospheric pressure. Cyclohexanol was continuously introduced into the reaction mixture at a rate of 12.2 gms. (0.122 mol.) per hour in order to maintain the reaction volume constant. 9.7 gms. (0.118 mol.) of cyclohexene were thus obtained per hour, representing a yield of 97% of the theoretical yield.

#### EXAMPLE 9:

Dehydration of cyclohexanol by phosphoric acid in the presence of acetic acid.

A mixture of phosphoric acid (60 gms.), pure acetic acid (212 cc.) and cyclohexanol (38 cc.), which proportions give rise to the maximum rate of reaction when employing acetic acid as the polar solvent, was heated to boiling point (155° C.) at atmospheric pressure. Cyclohexanol was continuously introduced into the reaction mixture at a rate of 229 gms. (2.29 mol.) per hour in order to maintain the reaction volume constant and cyclohexene was recovered at a rate of 182 gms. (2.25 mol.) per hour, representing a yield of 98.5% of the theoretical yield.

#### EXAMPLE 10:

Dehydration of cyclohexanol by phosphoric acid in the presence of monochloroacetic acid.

Initially, a mixture of cyclohexanol (125 cc.) and monochloroacetic acid (125 cc.) was introduced into a reaction vessel and the mixture was heated to boiling point (180° C.) at atmospheric pressure. After 3½ hours at this temperature, no cyclohexene had been formed.

20 gms. of  $H_3PO_4$  were then introduced into

- the reaction mixture and rapid formation of cyclohexene and water was observed. The reaction was continued at a temperature of 165° C., 257 gms. (2.57 mol.) of cyclohexanol being introduced per hour in order to maintain the reaction volume constant. Cyclohexene was thus obtained at a rate of 207 gms. (2.52 mol.) per hour, representing a yield of 98% of the theoretical yield.
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- 10 What we claim is:—
1. A method for the continuous production of olefinic compounds by the acid catalysed dehydration of alcohol in the liquid phase, wherein the dehydration is carried out in the presence of a polar solvent in which the alcohol to be dehydrated is soluble and which has a higher boiling point than that of water and of the olefinic compound produced.
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2. A method according to Claim 1, which comprises heating a mixture of an acid dehydrating catalyst, a polar solvent and an alcohol to boiling point, removing the reaction products by distillation, and continuously
- adding additional alcohol to the reaction mixture to maintain the reaction volume substantially constant.
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3. A method according to either claim 1 or 2, wherein the polar solvent is a phenol, a phenol derivative, a nitro-aromatic derivative, or acetic acid or a derivative thereof.
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4. A method according to Claim 3, wherein the polar solvent is phenol, cresol, xylene, nitrobenzene, nitrotoluene, monochloroacetic acid, dichloroacetic acid or a fluoroacetic acid.
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5. The method for the continuous production of olefinic compounds by the acid catalysed dehydration of alcohols in the liquid phase, wherein the dehydration is carried out in the presence of a polar solvent, substantially as herein described with reference to any one of the foregoing Examples.
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